A STUDY OF THE CHARRING OF DATONG COAL UNDER NITROGEN AND CARBON DIOXIDE ATMOSPHERES WITH PARTICULAR REFERENCE TO NANO-PARTICLE FORMATION

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ABSTRACT

Different chars are produced from Datong coal using thermo-gravimetric analyser having thermo-plus II software under different environments i.e. CO_2 and N_2 and different parametric conditions such as variations of temperature, flow rate etc. The produced chars are then subsequently analysed with field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (XPS) and Brunauer Emmett Teller (BET) surface area analyses in order to observe their structural properties. Thermo-gravimetric (TG) profiles of the produced chars are also presented and from these profiles it is observed that, at high temperatures and low flow rates, the weight loss percent of coal in CO_2 is higher than under an N_2 environment. This may be due to one additional step of coal gasification i.e. char gasification by CO_2 at higher temperatures. FESEM images show the formation of perfect hexagonal nanorod structures of char produced under CO_2 environment at a particular temperature of 773 K. Moreover, these images clearly show that, the amount and the dimension (size and shape) of nanorods are decreased and rods of smaller aspect ratio are observed with the increase of both flow rate and temperature as well. However, no such nanorods are observed when the char is produced under N_2 environment. Moreover, measured BET surface areas are also very high in CO_2 environment than N_2 environment which may be due to the greater exposure of internal surface area created by the char-CO_2 gasification reaction.

INTRODUCTION

Carbon nanoparticles have recieved tremendous scientific and industrial interests because of their peculiar properties and potential applications in functional nano-devices and environmentally clean energy purposes i.e. CO_2 capturing. Hence several different synthesis methods and carbon sources have been investigated for their production. Coal is a cheap, abundant in nature and a competent material for nanaoparticles production in large scale because of its advantages of itself usage as a purification medium of nanoparticles. Numerous studies have been found using coal as a source material for the production of nanoparticles using different methods [Pamh & Wilson, 1993; Qiu et al. 1998; Williams et al. 1999]. Plasma arcing is the most widely used process for the synthesis of nanotubes from coal [Iijima, 1991]. Arc-discharge method has also been employed to generate metal filled carbon nanotubes, nano-capsules, and the electronic structure and morphology of the metal inside the tube [Guerret-Plecourt et al. 1994; Saito et al. 1993]. Pang and Wilson (1993) reported the formation of carbon nanotubes from

coal and coke [Pang et al. 1995] after their successful attempts of fullerennes from coal [Pang et al. 1991; Pang et al. 1992]. Qiu et al. (1998) also reported the successful synthesis of carbon nanotubes and nano-capsules from Chinese coals using the similar process. Saito et al. (1994) reported SWNTs grwoing radially from Ni fine particles by the arcing evaporation of graphite carbon. Tian et al. (2001) produced nantubes from coal using Cu and Al as catalyst. They injected the coal into plasma jet directly, and the nanotubes were formed on the wall of the reactor.

Moreover, CO_2 have also been found a very attractive source material for nanoparticle production because of its various useful properties. It is a non toxic, less expensive, low energy, easily available and abundant molecule on earth. Some researchers used it in supercritical state [Kameo et al. 2003; Lou et al. 2006; Wong et al. 2007] and some others used in carbonate form [Lou et al. 2005] under different catalytic conditions using autoclave. Recently, Xu et al. 2007 used the horizontal fixed bed reactor for the production of nanotubes using CO_2 as a carbon source under the catalytic environment of Fe/CaO catalys. Removing, or scrubbing, the CO_2 may be as straight forward as turning the CO_2 into carbon nanospheres [Lou et al. 2006], nanotubes [Lou et al. 2005] or nanorods [Cao et al. 2008] either by the reduction of or by the pyrolysis reaction with CO_2 in the presence of metals [Lou et al. 2006; Lou et al. 2005; Cao et al. 2008]. Li et al. (2008) synthesized the carbon nanotubes by the pyrolysis of hydrocarbons and claimed that the presence of CO_2 enhanced the carbon nanotube formation [Li et al. 2008].

However, the combination of both coal and CO_2 as a carbon source for the production of nanoparticles has never been reported as yet. So the aim of this study is to produce nanoparticles using both cheap and easily available carbon sources in thermo-gravimetric analyzer which is a very simple and easy technique. TG profiles of the coal samples for char production and the FESEM images of the produced chars under N_2 and CO_2 environments at different temperatures and flow rates are also presented in this study. The experiments performed under different environments are for the implementation of the oxy-fuel combustion technology in future as differences in thermal properties of N_2 and CO_2 make oxy-fuel combustion quite different from conventional air combustion.

EXPERIMENTAL

Material and their Characterization

In the present study, a coal sample, imported from China (Datong coal), was first crushed, pulverized, sieved and then finally analyzed in TGA equipment using thermo-plus II software in order to analyze the coal sample. The surface area, pore volume and average pore diameter of the Datong coal are 5 m^2/g, 0.016 cm^3/g and 13.2 nm respectively. The proximate and ultimate analyses of the coal sample are summarized in Table 1.

Table 1: The proximate and ultimate analysis of Datong coal sample

Datong Coal Analysis			
Proximate analysis (%)		**Ultimate analysis (dry %)**	
Moisture	3.89	C	73.92
Volatile matter	27.28	H	3.82
Fixed carbon	61.54	O	10.24

Ash	11.18	N	0.27
		Total S	0.61
		Comb. S	0.57
		Un-comb. S	0.04
		Cl	90 (mg/kg)
		F	150(mg/kg)
		Na	470 (mg/kg)
		K	1600 (mg/kg)
		Hg	0.07 (mg/kg)
		Se	0.0001
		Cd	1 (mg/kg)
		As	0.0002
		B	0.0011

TGA measurement and analysis

TGA was employed due to its simplicity, cost effectiveness, and rapid analysis at below temperature i.e. 1273 K. The experimental procedure can be summarized as follows: about 10 mg of the sample having a particle size range of 50 -150 μm was placed in a quartz pan. The sample was packed loosely and placed in the pan over the TGA holder, of which one end was suspended and the other was attached to the microbalance. The temperature of the sample was measured by a thermocouple placed beneath the holder. The coal sample was heated from room temperature at a rate of 10 K/min to 773 K in a N_2 environment for one hour with a constant temperature of 773 K. The same experiment was performed under a CO_2 environment as well. The char samples were then analyzed for BET surface areas, FESEM and EDX analyses. FESEM (Auriga-39-22 FESEM) analyses was performed to see the structure of chars produced and observed the chars structural changes of nanorods which were formed during the reaction of coal with CO_2. In order to check the stability of nanorods, similar experiments were also performed but at relatively high temperature i.e. *c.a.* 1073 K. For all the experiments, the gas flow rate was kept at 50 cm^3/min. The weight change of the sample, time and temperature were recorded simultaneously for all the experiments using the thermo-plus II software.

RESULTS AND DISCUSSION

Results of Fig. 1(a, b) show the comparison of coal pyrolysis experiments in different gas environments *i.e.* CO_2 and N_2 up to 773 K pyrolysis temperature at a heating rate of 10 K/min in TGA. It can be clearly noted from Fig. that the weight loss percent of coal pyrolysis in the presence of N_2 is almost the same as that of pure CO_2 at 0 minutes of isothermal time *i.e. c.a.* 10% but with the passage of isothermal time from 0 to 90 min, the weight loss percent is found to be higher in case of CO_2 *i.e.* 24.34% at 90 min, than that of N_2 *i.e.* 21.45% at the same isothermal time. This difference may be better understood by analyzing the stages of the coal pyrolysis process for each environment. In case of 100% N_2 environment, the coal pyrolysis process has two stages: release of moisture content and devolatilization. However, the coal pyrolysis process in 100% CO_2 environment can be divided into three stages: moisture release, devolatilization and char gasification by CO_2 at high temperature zone [Li et al. 2009]. Also, this difference may be explained due to the density difference and transport properties of these gases which are quite different (the mass of the CO_2 molecule is different from that of N_2) and the

char surface area which is also higher than that of the N_2 char particles, as observed by Rathnam et al. (2009), hence the reduced weight observed in the CO_2 environment is higher than the N_2 environment. The use of 773 K as the pyrolysis temperature for this experiment is due to the fact that the ignition point of coal lies just above this temperature. In case of air, the ignition point is about 761 K and with same concentration of oxygen in oxy-fuel (21% O_2/79% CO_2), the ignition point is about 752 K.

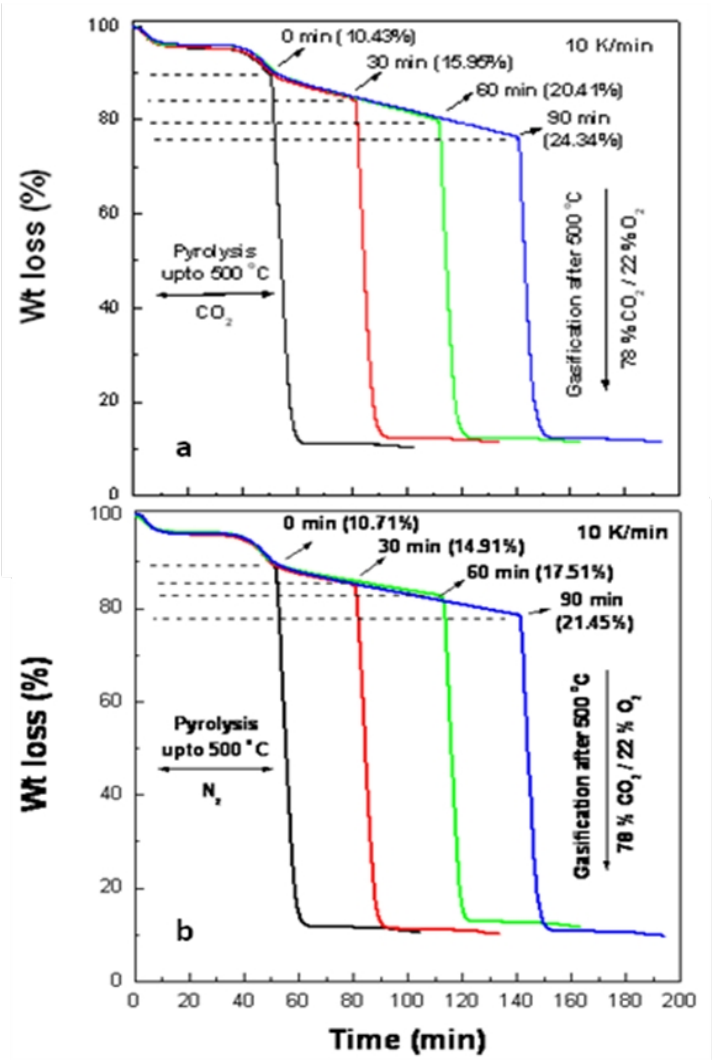

Fig 1: Weight loss percent of coal at different isothermal times under different environments at a heating rate of 10 K/min and flow rate of 50 cm^3/min (a) CO_2 (b) N_2.

Fig 2(a) shows the FESEM image of the original coal sample. The BET surface area of the original coal sample was found to be 5 m^2/g. However, after treating the coal samples with CO_2 and N_2, different structures of the char samples were obtained as shown in Fig 2 (b, c) i.e. Fig. 2 (b) and (c) show the FESEM images of the produced char under pure CO_2 and N_2 gas environments respectively for 1 h of isothermal time at 773 K. It was observed that, in case of CO_2, perfectly hexagonal nanorod structures were formed with a smooth surface of 200–300 nm in diameter and 2–3 μm in length. However, on the other hand, in case of N_2, a non-uniform structure of char was formed

and only a few large particles were present compared to the other nano-particles of size 200–300 nm as shown in Fig 2 (c).

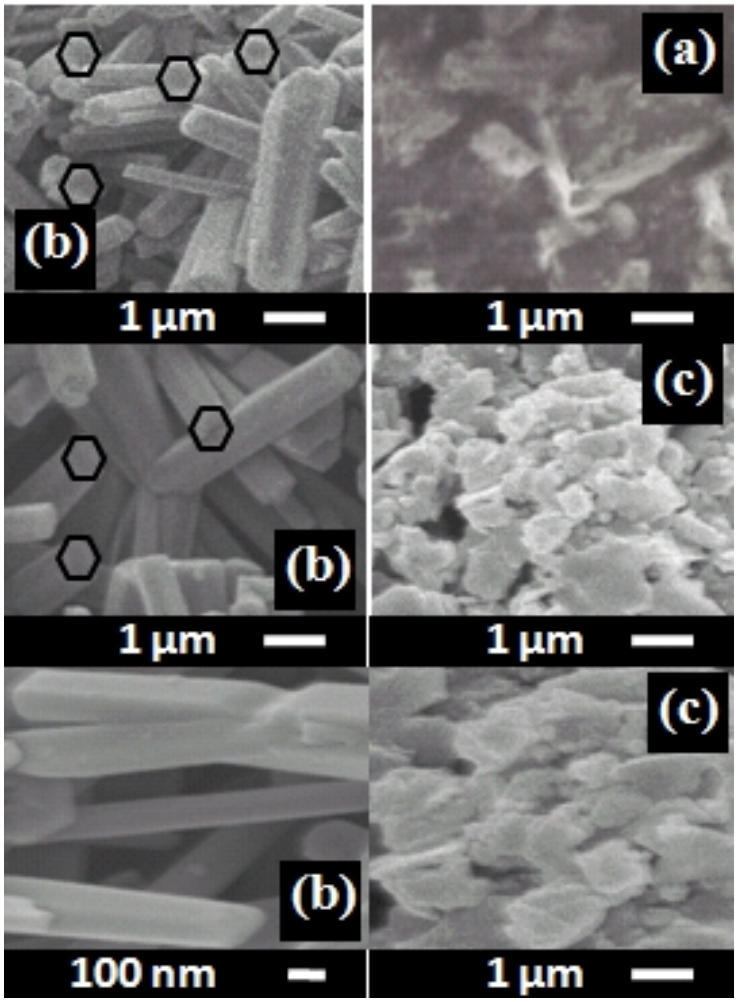

Fig 2; FESEM images (a) Original coal sample (b) Char sample produced under pure CO_2 gas for 1 h isothermal time at 773 K (c) Char sample produced under pure N_2 for 1 h isothermal time at 773 K.

It is noteworthy to mention that the formation of hexagonal nanorods were not observed when the sample was treated under N_2 atmosphere. Moreover, the BET surface areas of these char samples were also calculated and it was found that the surface area under the CO_2 environment was very high i.e. 400 m^2/g compared to the char produced under N_2 environment i.e. 52 m^2/g. This high surface area in case of CO_2 is probably due to the greater exposure of internal surface area created by the char-CO_2 gasification reaction [Rathnam et al. 2009] which subsequently results in the formation of hexagonal nanorods. Some additional experiments were also performed with different flow rates i.e. 50 cm^3/min and 75 cm^3/min under both CO_2 and N_2 environments at the same temperature of 773 K for 1 h isothermal time. It was observed that, under both gaseous environments, at high flow rate i.e. 75 cm^3/min, the weight rate loss was low but upon decreasing the flow rate i.e. 50 cm^3/min, the weight rate loss was increased due to longer residence time at lower flow rates (TG profiles are not shown).

The produced chars under different flow rates and different environments were again

analyzed using FESEM technique in order to see the effect of flow rates on nanorods formation and their structural changes. The Fig 3(a) and Fig 3(b) show the effects of 50 and 75 cm^3/min flow rates respectively on char production under N_2 environment. It can be clearly seen from Fig 3(a) that at lower flow rate of 50 cm^3/min less non-uniformity was observed having nanoparticles of 200 – 300 nm but unexpectedly few nano-rods were present having a size of diameter 200 – 300 nm and 1 – 2 μm in length. However, at 75 cm^3/min, greater non-uniformity was seen with nano-particles of two different types and sizes being observed having smaller particles of size 100 – 150 nm and the larger particles of size c.a. 500 – 700 nm.

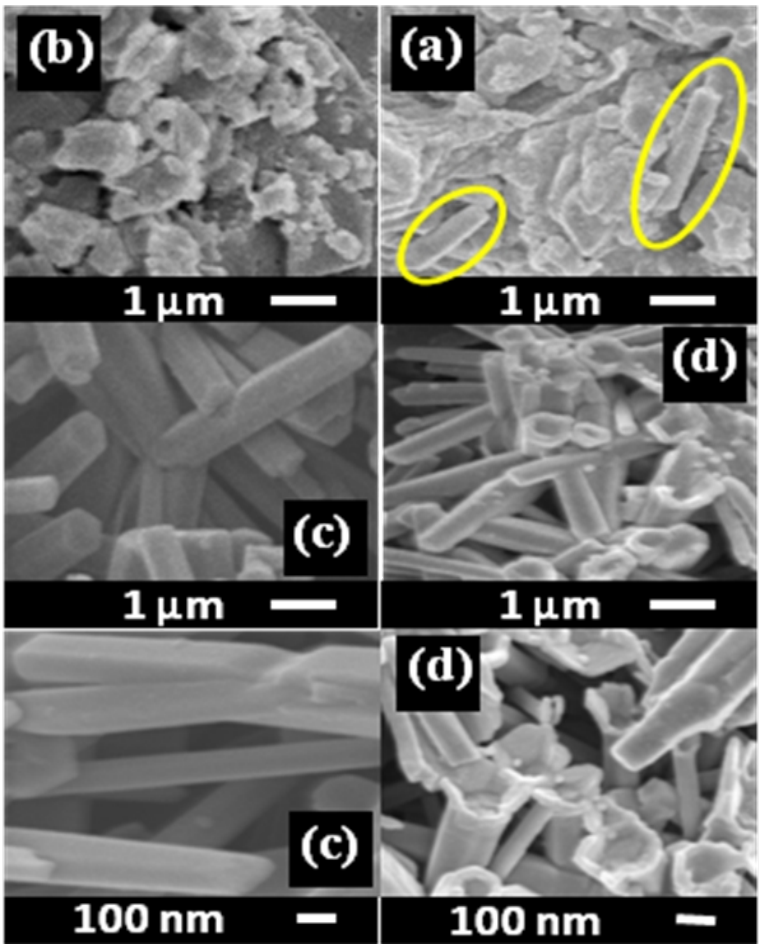

Fig 3: FESEM images of char produced at 773 K under different flow rates and different environments (a) N_2, 50 cm^3/min (b) N_2, 75 cm^3/min (c) CO_2, 50 cm^3/min (d) CO_2, 75 cm^3/min.

On the other hand, in case of CO_2, it was observed that at flow rate of 50 cm^3/min, perfectly hexagonal nanorods were formed with smooth surface of 200 – 300 nm in diameter and 2 – 3 μm in length. At flow rate of 75 cm^3/min, similar nanorods were observed with smooth surface of the same diameter but most of the rods were ruptured on one end due to the high flow rate and were shorter in length of 1 – 2 μm with less aspect-ratio compared with the rods of 50 cm^3/min. Moreover, the formation of nanorods at 50 cm^3/min were found to be higher in amount and large parts of the coal structure changed to nanorods compared with the least formation of nanorods at 75

cm3/min. This observation of the formation of perfect carbon hexagonal nanorods can be attributed to the reaction of CO_2 in the presence of some metals like alkali metals [Lou et al. 2006; Lou et al. 2005; Cao et al. 2008]. The proximate and ultimate analysis indicate the presence of metals such as Na, K, Se, Cd and As etc. in the coal sample which may act as catalysts for the formation of these hexagonal shaped nanorods. However, the EDX analysis indicates the presence of Al and Si metals in the char samples produced by the CO_2 and N_2 environments as shown below in the Table 2.

Table 2: EDX analyses of different chars produced in different environments at 50 cm^3/min flow rate and at 773 K

Elements	**N_2**		**CO_2**	
	Wt(%)	At(%)	Wt(%)	At(%)
C	73.50	81.77	72.84	79.86
O	15.35	12.82	20.80	17.12
Al	5.23	2.59	2.31	1.13
Si	5.92	2.82	4.05	1.90

This also indicates that these char samples consist mainly of C, O, Al and Si. However, the quantity of Al and Si in char is higher in the N_2 environment than in the CO_2 environment. Further, this analysis was done under the identical conditions as that of Fig 2.

Moreover, the coal sample was further reacted under CO_2 and N_2 environments at a heating rate of 10 K/min with a 50 cm^3/min flow rate but at a relatively high temperature i.e. 1073 K and kept it for 1 h at an isothermal condition under these gas streams. Again the results were same as that of Fig 1 i.e. the mass loss rate in CO_2 was found to be higher than that of the N_2 environment (TG figure is not shown). The produced chars were further analyzed by the FESEM in order to check the stability of these nano rods at high temperatures. In the case of N_2, at high temperatures i.e. 1073 K, high crystalline and rough outer surfaces were observed with the particle sizes of 200 – 500 nm, however, in the case of CO_2 at the same high temperature, the hexagonal shaped nanorods were broken down and converted into highly crystalline, smooth and uniform sized hexagonal nanoplatelets of sizes 100 nm as shown in Fig 4. The formation of these nanoplatelets indicates the destability of these hexagonal nanorod structures at higher temperatures.

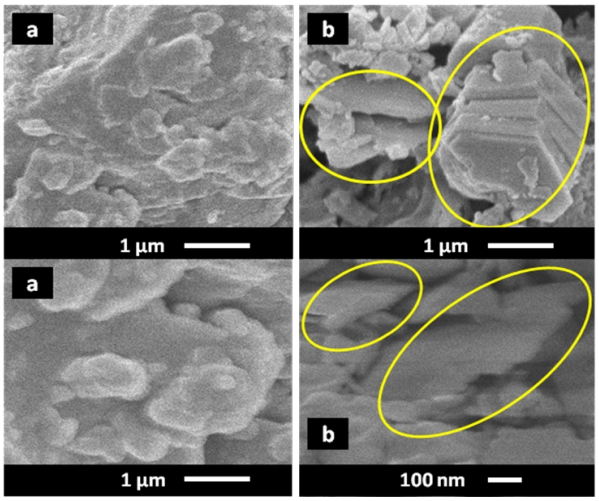

Fig 4: FESEM images of the char produced at 50 cm^3/min flow rate and at 1073 K (a) N_2 (b) CO_2.

CONCLUSIONS

In conclusion, char produced under different gaseous environments (N_2 and CO_2) and operational conditions i.e. temperature and flow rates are successfully compared using TGA and different analytical techniques. The results from FESEM analysis indicate that nanoparticles (hexagonal nanorods) are successfully formed under the CO_2 environment. However, no such nanorods are formed under N_2 environment. The formation of these nanorods are due to the presence of metals such as Na, K etc. present inside the coal sample which may act as a catalyst. In case of CO_2, the char produced is converted mostly into nanorods with smooth surfaces at lower flow rate but upon increasing the flow rate, small numbers of nanorods are formed indicating the non-uniformity in the char sample. Moreover, these produced nanorods are equivalent in diameter but smaller in length i.e. having a lower aspect-ratio than the rods produced at lower flow rates. Similarly, in case of N_2, greater non-uniformity appears at high flow rates compared with lower flow rates. Moreover, at high temperature i.e. 1073 K, the nanorods are broken down and converted into nano platelets due to the rupturing of nanorods indicating the de-stability of nanorods at high temperatures.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support received in the form of a research grant i.e. UMRG (RG095/10AET) by the University of Malaya, Malaysia.

REFERENCES

Cao, F, Liu, Y, Hu, W & Chen, Q 2008, Morphogenesis of branched coaxial nanorods formed in supercritical carbon dioxide, *J. Phys. Chem. C.*, vol. 112, pp. 2337 – 42.

Guerret-Plecourt, C, Bouar, YL, Lolseau, A & Pascard, H 1994, Relation between metal electronic structure and morphology of metal compounds inside carbon nanotubes, *Nature*, vol. *372*, pp. 761 – 4.

Iijima, S 1991, Helical microtubules of graphitic carbon, *Nature*, vol. 354, pp. 56 – 58.

Kameo, A, Yoshimura, T & Esumi, K 2003, Preparation of noble metal nanoparticles in supercritical carbon dioxide, *Physicochemical & Engg. Aspects* vol. 215, pp.

181–189.
Li, Z, Xu, Y, Ma, X, Dervishi, E, Saini, V, Biris, AR et al. 2008, CO_2 enhanced carbon nanotube synthesis from pyrolysis of hydrocarbons, *Chem. Commun*, pp. 3260 – 62.
Li, Q, Zhao, C, Chen, X, Wu, W & Li, Y 2009, Comparison of pulverized coal combustion in air and in O_2/CO_2 mixtures by thermo-gravimetric analysis, *J. Anal. Appl. Pyrol.*, vol. *85*, pp. 521 – 28.
Lou, Z, Chen, C, Zhao, D, Luo, S & Li, Z 2006, Large-scale synthesis of carbon spheres by reduction of supercritical CO_2 with metallic calcium, *Chem. Phys. Lett.*, vol. 421, pp. 584 – 88.
Lou, Z, Chen, C, Chen, Q & Gao, J 2005, Formation of variously shaped carbon nanotubes in carbon dioxide–alkali metal (Li, Na) system, *Carbon*, vol. 43, pp. 1084 – 14.
Pang, LSK & Wilson, MA 1993, Nanotubes from coal, *Energy Fuels*, vol. 7, pp. 436 – 47.
Pang, LSK, Prochazka, L, Quezada, RA, Wilson, MA, Pallasser, R, Fisher, KJ, Fitzgerald, JD, Taylor, GH, Willett, GD & Dance, IG 1995, Competitive reactions during plasma arcing of carbonaceous materials, *Energy Fuels*, vol. *9*, pp. 38 – 44.
Pang, LSK, Vassallo, AM & Wilson, MA 1991, Fullerenes from coal, *Nature*, vol. *352*, pp. 480 – 90.
Pang, LSK, Vassallo, AM, Wilson, MA 1992, Fullerenes from coal: a self-consistent preparation and purification process, *Energy Fuels* vol. *6*, pp. 176 – 9.
Qiu, JS, Zhou, Y, Wang, LN & Tsang, SC 1998, Formation of carbon nanotubes and encapsulated nanoparticles from coals with moderate ash contents, *Carbon*, vol. 36, pp. 465 – 77.
Rathnam, RK, Elliott, LK, Wall, TF & Liu, Y 2009, Moghtaderi, B. Differences in reactivity of pulverized coal in air (O_2/N_2) and oxy-fuel (O_2/CO_2) conditions, *Fuel Proc. Tech.*, vol. 90, pp. 797 – 02.
Saito, Y, Yoshikawa, T, Okuda, M, Fujimoto, N, Sumiyama, K, Suzuki, K, Kasuya, A & Nishina, Y 1993, Carbon nanocapsules encaging metals and carbides, *J. Phys. Chem. Solids*, vol. *54*, pp. 1849 – 60.
Saito, Y, Okuda, M, Fujimoto, N & Yoshikawa, T 1994, Single-wall carbon nanotubes growing radially from Ni fine particles formed by arc evaporation, *Jpn. J. Appl. Phys.* vol. *33*, pp. L526 – L529.
Tian, YJ, Xie, KC & Fan, YS 2001, *Chem J Chin Univ-Chin* vol. *22*, pp. 1456 – 58.
Williams, KA, Tachibana, M, Allen, JL, Grigorian, L, Cheng, SC, Fang, SL, Sumanasekera, GU, Loper, AL, Williams, JH, Eklund, PC 1999, Single-wall carbon nanotubes from coal, *Chem. Phys. Lett.* vol. 310, pp. 31 – 7.
Wong, B, Yada, S & Howdle, S 2007, The preparation of gold nanoparticle composites using supercritical carbon dioxide, *The J. Supercritical Fluids*, vol. 42, pp. 282 – 87.
Xu, X & Huang, S 2007, Carbon dioxide as a carbon source for synthesis of carbon nanotubes by chemical vapor deposition, *Mat. Lett.*, vol. 61, pp. 4235 – 37.

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